Elementary Determination of the Superficial Amount of —OH on Poly(vinyl alcohol) Film by Titration and X-Ray Photoelectron Spectroscopy

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ABSTRACT: The hydroxyl group (—OH) is the exclusive functional group of poly(vinyl alcohol) (PVA), and there must be abundant hydroxyl groups on its surface. This study determined the superficial hydroxyl group amount of PVA (degree of polymerization = 1700 $\pm$ 50, degree of alcoholysis $\geqslant$ 99.0%) by a chemical method (titration) and an instrumental method [X-ray photoelectron spectroscopy (XPS)]. The results showed the following: (1) the order of magnitude of its superficial hydroxyl group amount was about 3.8×10^{-5} mol/cm^2 by the acylation method with a single functional group reagent (acetic anhydride); (2) the hydroxyl group amount outcome by the esterification method with a bifunctional group reagent (toluene-2,4-diisocyanate) was much lower than that by the acylation method (ca. 7.74×10^{-7} mol/cm^2); and (3) the relative content of oxygen on the PVA surface given by XPS surface analysis was 22% of the total, which was lower than that of the theoretical amount (36%). On the basis of the results, it was shown that the number of available or free hydroxyl groups was less than theoretical amounts. Although there was a difference among the outcomes, it could be useful for providing a quantitative reference when the hydroxyl group on a solid PVA surface is used for surface modification; moreover, the outcomes and differences also offer us knowledge of the surface modification efficiency. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 584–588, 2008

Key words: polyvinyl alcohol; XPS; hydroxyl group amount; biopolymers; drug delivery systems; interfaces; surfaces

INTRODUCTION

Poly(vinyl alcohol) (PVA) is a multipurpose polymer characterized by low toxicity[1–4] and noncausticity and biodegradability,[5] and its applications have been extensively expanded to many fields, such as fiber terylene manufacturing, emulsifiers, films, foods, paints, adhesives, medicine, and biomaterials.[6–14] PVA sometimes needs hydrophobic modification for some applications because of its excellent hydrophilicity, and there should be innumerable hydroxyl groups on its surface, use of which could be made of for surface modification to improve its performance or expand its application fields. When PVA needs surface modification, the only available functional group is the hydroxyl group; however, how many hydroxyl groups exist on its surface is still unknown.

A traditional standard method for determining the content of hydroxyl groups has been developed that is based on the mechanism of acylation between acid anhydride and hydroxyl groups. Because of the differences among the acid anhydride, catalyst, and reaction media, more than 10 similar methods have been developed for the assay of hydroxyl groups.[15,16] Now, X-ray photoelectron spectroscopy (XPS) analysis is increasingly used for surface analysis.[17–20] In this study, we assayed the superficial hydroxyl group amount of PVA film by a chemical method (titration) and an instrumental method (XPS) to provide a quantitative reference when the superficial hydroxyl group of PVA is to be used for surface modification, and the outcomes also offer us knowledge of the surface modification efficiency.

EXPERIMENTAL

Main reagent and instruments

PVA (PVA-1799; degree of polymerization = 1700 $\pm$ 50, degree of alcoholysis $\geqslant$ 99.0%), toluene-2,4-diisocyanate (TDI), anhydrous sodium acetate, glacial acetic acid, 0.01M and 1.0M standard sulfuric acid solutions, a 1.0M standard sodium hydrate solution, n-butylamine (analytical purity for all reagents), and potassium biphthalate (standard reagent) were used.

An acid/alkali buret, iodine flask, conical flask, pH meter, micrometer/spiromicrometer, and XPS (XSAM800, Kratos Co., Manchester, Great Britain) were used.

Preparation of the PVA film

A PVA-1799 granule was immersed in 10-fold or more warm distilled water (37–50°C) for preswelling for 2 h, and then the temperature was quickly raised over 94°C so that PVA-1799 could be quickly dissolved in boiling water with slow agitation ($\approx$90 r/min) to prepare an aqueous PVA solution. The PVA solution was spread on a flat glass slab to cast the PVA film, and then the liquid PVA film was first air-dried at room temperature and then oven-dried at 60°C or so for 2 h. Finally, the dried PVA film was cut into small rectangles with each side less than 10 mm.

Preparation of the reagent

0.01M and 1.0M standard sulfuric acid solutions and 1.0M standard sodium hydrate solution

The solutions were prepared according to GB601.88. The concentration of the H_2SO_4 solution was standardized to $C_1(H^+) = 0.01812$ mol/L and $C_2(H^+) = 1.1020$ mol/L, respectively; the concentration of NaOH was 0.9838 mol/L.

n-Butylamine solution

1,4-Dioxane was prepurified by the addition of potassium hydroxide and then distilled the next day. Redistilled n-butylamine (5.0 mL) was pipetted into a 1000-mL volumetric flask and then diluted to 1000 mL with purified 1,4-dioxane.

Determination of the hydroxyl group amount

Acylation method[21]

Each sample contained pieces of a small, rectangular PVA film. The total area of each sample was calculated as follows (see Fig. 1):

$$S = \sum_{i=1}^{n} S_i [n \leq 30, S_i = 2LW + 2(L + W)h]$$

where S is the total area of each PVA film sample, and each sample has 20–30 pieces of rectangle PVA film; S_i is the total area of each piece of rectangle PVA film, n is the number of pieces of rectangle PVA film. L is the length, W is the width, and h is the height. The total mass of each sample was m_0.

The assaying process was as follows. First, the sample and 1.00 g of anhydrous sodium acetate
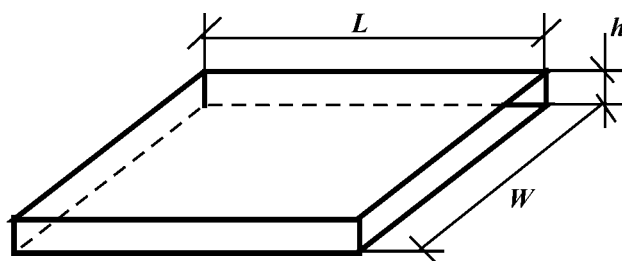

Figure 1 Area calculation of the PVA film.

were added to a dried 500-mL conical flask. Second, the flask was jiggled lightly to mix the PVA film with anhydrous sodium acetate. Third, 5 mL of acetic anhydride (excess) was pipetted into the flask; this was followed by light jiggling of the flask to mix anhydrous sodium acetate with acetic anhydride. Fourth, the conical flask was heated slowly to boiling; when the backstreaming from the bottom went up three quarters of the flask, the flask was taken away from the heater and allowed to cool to room temperature. Fifth, 25 mL of tridistilled water was added to the flask, and the flask was taken away to cool to room temperature when the solution was re-heated to boiling. Sixth, 8 drops of 1% dihydroxyphthalophenone indicator was added to the flask, and this was followed by slow neutralization with 1.0M NaOH until the color of the solution approached plum; at this time, a pH meter was used to monitor the pH. The end point of titration was when the pH rose to 9.7. Seventh, 20.0 mL of 1.0M NaOH was added to the solution, and then the solution was re-heated to boiling for 10 min; when the heating time was up, the flask was taken away, and the alkali asbestos tube was immediately put into the flask mouth for sealing. Finally, the solution was cooled to room temperature quickly in ice water. Eighth, the fifth step was repeated, the solution was titrated with 1.0M H_2SO_4, and then the volume of H_2SO_4 consumed was recorded. Ninth, steps 2–9 were repeated for the blank test, and then the volume of H_2SO_4 consumed was also recorded.

Esterification method[22]

Because the reagent used in the acylation method is one with a single functional group, in most cases, coupling reagents are used to link the objective molecule onto the surface of the matrix. For example, an enzyme can be immobilized onto a matrix to prepare immobilized enzymes with the link of a coupling reagent. To investigate the efficiency between the superficial hydroxyl group of PVA and a coupling reagent with a multifunctional group (mainly a bifunctional group reagent), another assay system was designed for further study.

TABLE I
Results of the Acylation Method

Item	Sample				
	1	2	3	4	5
S_{PVA} (mm^2)	4246.83	3151.98	3548.41	4197.57	3637.12
$\overline{V}_0$ (mL)			17.35		
$C_{\frac{1}{2}H_2SO_4}$ (mol/L)			1.1020		
$V_{\frac{1}{2}H_2SO_4}$ (mL)	15.40	16.40	16.50	16.00	15.88
C_{PVA-OH} ($\times10^{-5}$ mol/cm^2)	5.06	3.32	2.64	3.54	4.45
$\overline{C}_{PVA-OH}$ ($\times10^{-5}$ mol/cm^2)			3.80		
m_{PVA} (g)	0.5934	0.5873	0.6245	0.8371	0.5616
$C_{PVA-OH(total)}$ (mol)	0.01349	0.01335	0.01419	0.1902	0.01276
R (%)	15.93	7.84	6.60	7.81	12.68

C_{PVA-OH} = the content of superficial hydroxyl group of PVA; $\overline{C}_{PVA-OH}$ = the average content of superficial hydroxyl group of PVA; $C_{PVA-OH(total)}$ = the total content of hydroxyl group of PVA; m_{PVA} = the total mass of PVA films; $\overline{V}_0$ = the average volume of blank test.

The procedure was as follows. First, the total area of each sample was calculated as shown in Figure 1; then, the sample was added to a dried flask, and the addition of 200 mL of purified anhydro-1,4-dioxane, 20 mL of TDI (excess), and 200 µL of dilaurostearic acid dibutyl tin as a catalyst followed. Finally, the system was allowed to hermetically react for 6 h at 60°C. Second, when the reaction time was up, the PVA films were taken out and immediately washed in purified anhydrous acetic ether five to eight times; then, the films were quickly dried in air to volatilize acetic ether away, and finally, the films were added to a dried iodine flask. Third, a 10.0-mL n-butylamine solution was immediately added to the iodine flask, and its plunger was immediately put into its mouth for sealing. Fourth, the flask was jiggled slightly to let an n-butylamine solution soak the films for 1 min, and then the system was allowed to react at room temperature with slight shaking for 15 min. Fifth, when the reaction time was over, 10 mL of distilled water was added to the iodine flask mouth; then, the plunger was drawn out slowly to let the water run down along the flask wall. After the process was repeated twice, the plunger was taken away. Sixth, 2 drops of 1% dihydroxyphthalophenone indicator were added to the solution, which was then titrated with 0.01M H$_2$SO$_4$ up to the emergence of a steady red color in the solution. The volume of H$_2$SO$_4$ consumed was recorded. Seventh, steps 3–6 were repeated for the blank test, and the volume of H$_2$SO$_4$ consumed was recorded.

XPS surface analysis

To further the analysis from another point of view, surface analysis (XPS) was conducted by XSAM800; the scanning area was 8 mm × 8 mm, and the sample was the same as that mentioned in the Preparation of the Reagent section. The analytical parameters were as

follows: analyzer mode, FAT; magnification, low; energy range, ×1; exciting source, Mg; and number of down scans, two.

RESULTS AND DISCUSSION

Results of the acylation method

The results are given in Table I. The order of magnitude of the superficial —OH amount was about 3.8×10^{-5} mol/cm^2. On the basis of the cast film, from the R parameter, it was calculated that the content of —OH on the surface given by this method was about 10% of the total.

Results of the esterification method

The results are given in Table II. The order of magnitude of the superficial —OH amount outcome by the esterification method was much less than that by the acylation method (ca. 7.7×10^{-7} mol/cm^2).

TABLE II
Results of the Esterification Method

Item	Sample				
	1	2	3	4	5
S_{PVA} (cm^2)	80.5	86.3	97.6	124.5	76.4
$V_{\frac{1}{2}H_2SO_4}$ (mL)	6.32	6.02	5.21	5.14	6.92
$C_{\frac{1}{2}H_2SO_4}$ (mol/L)			0.01812		
$\overline{V}_0$ (mL)			9.88		
$C_{TDI-NCO}$ ($\times10^{-5}$ mol)	6.45	6.99	8.46	8.59	5.32
C_{PVA-OH} ($\times10^{-7}$ mol/cm^2)	8.01	8.10	8.67	6.90	7.02
$\overline{C}_{PVA-OH}$ ($\times10^{-7}$ mol/cm^2)			7.74		

C_{PVA-OH} = the content of superficial hydroxyl group of PVA—OH; $\overline{C}_{PVA-OH}$ = the average content of superficial hydroxyl group of PVA; $C_{TDI-NCO}$ = the content of isocyanate group of TDI; $\overline{V}_0$ = the average volume of blank test.
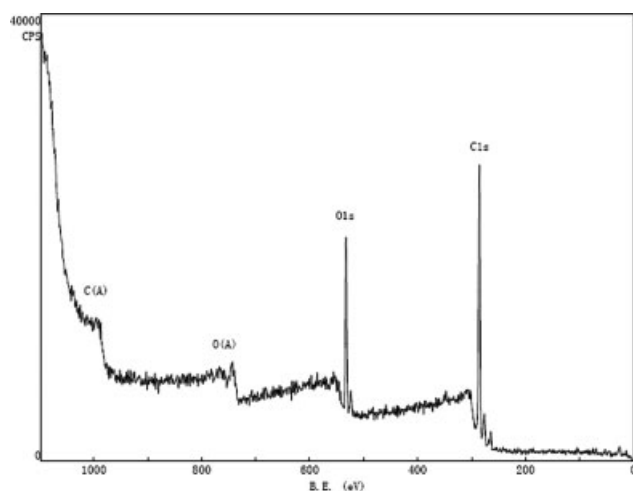
Figure 2 XPS image of the PVA-1799 film scanned by XSAM800 (B.E. = binding energy).

Results of the XPS analysis

The XPS spectrum of the PVA-1799 surface is presented in Figure 2. From the spectrum, it can be seen that the surface chemical elements of PVA consist mainly of oxygen and carbon; automatically integrating the area of the oxygen peak and carbon peak by XPS resulted in 12,660.2 and 44,358.8, so the relative content of the oxygen element in the PVA surface was up to 22% [12,660/(12,660 + 44,358)] of the total.

DISCUSSION

The physical properties of PVA are certainly steady; it is easily dissolved in water (especially boiling water) but is insoluble and unswollen in any organic solvent. Its chemical properties are also very inactive, and it is tolerant of acids, alkalis, and oxidation; its hydrophilicity and biocompatibility are also very excellent, and all of these advantages make it a multipurpose polymer.

As shown in Table I, according to parameter R, it could be calculated that the —OH content on the surface of the PVA film took up about 10% of the bulk, and it also could be inferred that most —OH in the bulk other than that on the surface became null functional groups and did not react with the reagent because PVA is insoluble and unswollen in organic solvents, so organic reagent molecules could not permeate the bulk of PVA to react with —OH in the interior. If PVA were swollen or dissolved in an organic solvent, the excess reagent could permeate and react with —OH in the bulk, so all values of R should be 100%. However, the outcomes showed that all R values were not 100% but instead 10% or so, and this proved that organic molecules could not permeate the PVA bulk. Furthermore, it was obvious that the concentration of PVA—OH had a higher

dispersion, and this may have happened for two possible reasons: the operational error or heterogeneity of the reaction between the solid and liquid or the local heterogeneity of the —OH distribution on the surface of the PVA film. All this results in the difference of the —OH amount with the same surface area. On the basis of the outcomes, a hypothesis could be made: if a single functional group molecule were immobilized on a PVA surface to develop a kind of adsorbing material with PVA as a supporter, the theoretical maximum capacity of the molecules immobilized onto the PVA surface could be predicted only if the specific surface area of PVA were known.

As for the esterification system, theoretically, one TDI bears two active —NCO's, one —NCO reacts with one —OH, and the other —NCO will wait to react with n-butylamine; thus, the amount of —OH could be indirectly known by the determination of the content of —NCO. According to Table II, the outcome for the amount of —OH (7.74×10^{-7} mol/cm^2) by the esterification method with a bifunctional group reagent (TDI) was much lower than that by the acylation method; it was also seen that the concentration of PVA—OH had a lower dispersion degree and a higher precision degree. The reason may be the improvement of the homogeneity and sufficiency of the reaction system due to the existence of a solvent (1,4-dioxane).

There were different outcomes between the two assay systems with respect to the results. The reasons may be as follows: (1) parts of two —NCO's in one TDI molecule reacted with —OH; (2) a stereospecific blockade effect prevented all the superficial —OH from reacting with —NCO; and (3) the reaction efficiency of the esterification method was lower than that of the acylation method, and this resulted in the reduction of detectable —NCO and a different outcome. Besides, the difference may have been caused by the difference in the natures of the two systems. In this case, it could be inferred that using another bifunctional group reagent or changing the reaction time or temperature may lead to a different outcome. On the basis of this difference, it may enlighten us that the ratio of reactants, the reaction time, or both play a very important role in modification effectiveness when a coupling agent is used, and it could be unavoidable that parts of the coupling agent and functional groups on the matrix must become null ones. The difference also proves the fact that the simpler the reagent is and the fewer reaction steps there are, the higher the reaction efficiency is, the greater the homogeneity of the reaction system is, and the higher the efficiency is.

The outcome given by XPS analysis showed that the relative content of the oxygen element on the surface of the PVA film was up to 22% of the total,

but the theoretical content of oxygen (only originating from —OH) in PVA is 36%. If all the —OH's on the PVA surface were exclusively naked outwards, the relative content of the oxygen element determined by XPS should be 36% or so; however, there still exists a difference between the outcome and the theoretical amount, and this indicates that a only small number of —OH's on the PVA surface are completely naked outwards, and the others are partly naked or included. Therefore, the results given by XPS analysis confirm the fact that the content of —OH that is naked outwards on the PVA surface is not as much as the theoretical content. It is a pity that the technique of XPS analysis cannot give the absolute content of chemical elements on a material's surface but can give only the relative content.

The unit for results by XPS is percentage, whereas the unit for results given by the chemical method is moles per centimeter squared; therefore, the comparison of XPS results with chemical results is not possible because the two different units cannot be interconverted. Superficially, the XPS analysis seems to be of no use for the assay of the —OH amount, but the XPS outcome tells us that the —OH amount available is less than the theoretical amount. From the results given by two different analytical methods, it might at least be concluded that the effective/active amount of —OH on the PVA surface is far less than the theoretical amount; in addition, the reaction efficiency usually cannot reach 100%, and a side reaction usually exists. All of the adverse factors contribute to the fact that the modification efficiency and immobilized amount are usually very low, and the results in this study also provide evidence for the fact.

CONCLUSIONS

This study determined the superficial —OH amount of PVA-1799 by two chemical methods and XPS analysis. Although the result may show a certain deviation from the theoretical amount because of many influential factors, it offers us knowledge of the superficial —OH amount of PVA and a concept of surface modification efficiency. The result would be useful for providing a quantitative reference when superficial —OH of PVA is used for surface modification for some application.

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